Letter

Efficient heterogeneous oxidation of organosilanes to silanols catalysed by a hydroxyapatite-bound Ru complex in the presence of water and molecular oxygen

Kohsuke Mori, Makoto Tano, Tomoo Mizugaki, Kohki Ebitani and Kiyotomi Kaneda*

Department of Chemical Science and Engineering, Graduate School of Engineering Science,
Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.
E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81-6-6850-6260
Tel: +81-6-6850-6260

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RuHAP is a highly selective and reusable catalyst for the oxidation of a wide variety of organosilanes to the corresponding silanols in the presence of water and molecular oxygen.

Silanols are utilized in industry as valuable building blocks for silicon-based polymeric materials, which are generally synthesized by hydrolysis of halosilanes, stoichiometric oxidation of organosilanes, and reaction of siloxanes with alkali reagents.[1] These procedures often result in the production of vast amounts of environmentally damaging wastes. Highly efficient catalytic transformation of silanes to the corresponding silanols is therefore particularly attractive from both environmental and synthetic perspectives. Some homogeneous transition metal complexes such as $[RuCl_2(p\text{-cymene})]_2$ and methyltrioxorhenium have been found to catalyze oxidation of silanes,[2,3] but often demonstrate limited practical utility due to difficulties in catalyst separation and recovery.

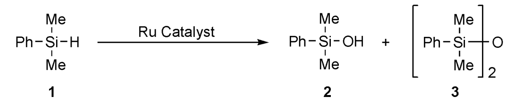
Hydroxyapatites, the main component of bones and teeth, are of considerable interest in many areas because of multiple functionalities including ion-exchange ability, adsorption capacity, and acid-base properties.[4] Recently, we reported that monomeric Ru cation species could be uniformly introduced into the hydroxyapatite surface based on a cation-exchange process.[5a] This hydroxyapatite-bound Ru complex (RuHAP) exhibits excellent catalytic performances for the aerobic oxidation of alcohols and *primary* amines, attributable to a monomeric Ru species as the phosphate complex on solid surfaces.[5] In the course of our ongoing studies for exploring practical organic transformations using RuHAP, we also found that oxidation of silanes occurred smoothly to give the corresponding silanols. The catalytic system described here is a powerful candidate for a promising synthetic protocol because of the following advantages: (1) use of the nonpolluting oxidants of water and molecular oxygen, (2) high selectivity and substrate tolerance, (3) stereospecific oxidation *via* inversion of the configuration of silanes, and (4) simple work-up procedure and easy recovery of catalyst.

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, was synthesized as reported previously.[6] Calcium hydroxyapatite (1 g) was stirred at 25 °C for 24 h in 100 mL of a 1.0×10^{-2} M aqueous $RuCl_3 \cdot nH_2O$ solution. The obtained slurry was filtered, washed with deionized water, and dried overnight at 110 °C, yielding RuHAP as a dark brown powder (Ru content: 0.97 $mmol \cdot g^{-1}$). Characterization by elemental analysis, XPS, EDX, and Ru-K edge XAFS revealed that the Ru species exists as a monomeric Ru^{3+} cation surrounded by four oxygen atoms and one chlorine atom.[5a]

As shown in Table 1, oxidations of dimethylphenylsilane (**1**) using various Ru catalysts were carried out under several sets of conditions. The RuHAP catalyst exhibited the highest activity in the presence of water under atmospheric oxygen to afford the corresponding dimethylphenylsilanol (**2**) in 99% yield (entry 1). Water and molecular oxygen were indispensable components for attaining high silanol yields (entries 2 and 3). Among the solvents examined, ethyl acetate, acetonitrile, and DMF were excellent solvents, while *n*-heptane and toluene gave poor results with respect to both conversion and selectivity. Typical heterogeneous Ru catalysts such as Ru/carbon, RuO_2, and Ru/Al_2O_3 were found to be less effective under the same reaction conditions. The use of $Pr_4N^+ \cdot RuO_4^-$ and $RuCl_3 \cdot nH_2O$ led to silanol condensation, giving an undesirable disiloxane (**3**).

Oxidation results for a variety of silanes catalyzed by the RuHAP under optimal reaction conditions are summarized

Table 1 Oxidation of dimethylphenylsilane using various Ru catalysts[a]



Entry	Catalyst	H_2O (equiv.)	Atmosphere	Conv./ %[b]	Selectivity[b] **2:3**
1	**RuHAP**	**5**	**O_2**	**>99**	**>99:1**
2	RuHAP	–	O_2	<1	–
3	RuHAP	5	Ar	7	>99:1
4	Ru/carbon[c]	5	O_2	97	73:27
5	RuO_2[c]	5	O_2	84	70:30
6	Ru/Al_2O_3[c]	5	O_2	66	64:36
7	$RuCl_2(PPh_3)_3$	5	O_2	94	56:44
8	$Pr_4N^+ \cdot RuO_4^-$[d]	5	O_2	47	10:90
9[e]	$RuCl_3 \cdot nH_2O$[c]	5	O_2	48	3:97

[a] Reaction conditions: dimethylphenylsilane (1 mmol), ethyl acetate (5 mL), Ru catalyst (5 mol % of Ru relative to substrate), 80 °C, 3 h. [b] Determined by GC using an internal standard technique. [c] Purchased from N.E. Chemcat. [d] Purchased from Aldrich. [e] Acetonitrile was used as the solvent.

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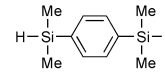
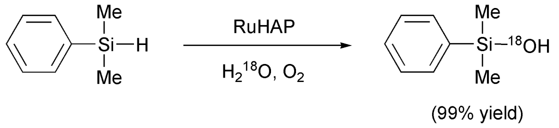
Table 2 RuHAP-catalysed oxidation of silanes in the presence of H_2O and O_2[a]

Entry	Substrate	Time/h	Conv./%[b]	Yield/%[b]
1	$PhMe_2SiH$	3	100	99
2	Recycle 1	3	100	97
3	Recycle 2	3	100	98
4	Recycle 3	3	100	97
5	Recycle 4	3	100	98
6[c]	t-$BuMe_2SiH$	24	89	89
7	Ph_2MeSiH	12	95	92
8	Et_3SiH	6	93	92
9	$(n\text{-}Bu)_3SiH$	12	100	> 99
10	$(n\text{-}C_6H_{13})_{13}SiH$	12	92	90
11	$\mathrm{Ph{-}{\equiv}{-}SiMe_2H}$	14	92	92
12	$\mathrm{Ph{-}{=}{-}SiMe_2H}$	12	93	90
13	Ph_2SiH_2	9	100	98[d]
14		24	91	91[d]

[a] Reaction conditions: silane (1 mmol), ethyl acetate (5 mL), RuHAP (0.05 g, Ru: 0.05 mmol), H_2O (5 mmol), 80 °C, O_2 atomsphere. [b] Determined by GC analysis using an internal standard technique. [c] H_2O (3 mmol), 70 °C. [d] Isolated yield.

in Table 2. In our oxidation system, the corresponding silanols were obtained without any condensation products. For example, even the sterically exposed silane of triethylsilane was exclusively oxidized to give triethylsilanol in 92% yield (entry 8). Generally, silanols containing small substituents are easily converted to the disiloxane due to heat, acid, or base instability, which is a crucial drawback in other reported synthetic procedures.[1,7] The RuHAP catalyst was also applicable to the oxidation of silanes possessing alkynyl and alkenyl groups to form the corresponding silanols in high yields (entries 11 and 12). In the cases of diphenylsilane and 1,4-bis(dimethylsilylbenzene), the silanediols were obtained in almost quantitative yields (entries 13 and 14). Sterically bulky silanes such as triphenylsilane and triisopropylsilane were hardly oxidized under the present system. The RuHAP catalytic system represents a highly suitable method for large-scale operations; a 100 mmol scale oxidation of **1** was completed within 6 h to provide 94% of **2**. Growing interest has been shown in the synthesis of optically active silanols as useful synthetic intermediates for a variety of bioactive compounds.[8] *More significantly, the RuHAP-catalyzed oxidation of optically active silanes proceeded exclusively with inversion of the silicon configuration*; the oxidation of (+)-methylethylphenylsilane in the presence of RuHAP, followed by reduction with $LiAlH_4$, afforded (−)-methylethylphenylsilane in 97% *ee*.† Similar stereospecific oxidation has also been achieved with the $[RuCl_2(p\text{-cymene})]_2$ complex, but the selectivity with RuHAP was higher than that reported for the homogeneous Ru complex.[2] Such a prominent performance of RuHAP might be due to the structurally robust monomeric active site on a solid surface, which provides strict steric control of the reaction intermediate. XAFS analysis revealed that no structural changes around the Ru^{3+} center were observed after the oxidation.‡ In the oxidation of dimethylphenylsilane, the catalyst was filtered off after *ca.* 50% conversion at the reaction temperature. The filtrate was further reacted at 80 °C for 3 h and no oxidation of dimethylphenylsilane occurred. Ru leaching in the filtrate was not observed by ICP analysis, whose detection limit is 0.04 ppm. It can be said that this silane oxidation proceeds with heterogeneous Ru species. Furthermore, the RuHAP catalyst could be reused four times without loss of the high catalytic activity and selectivity (entries 2–5).



Scheme 1 Reaction conditions: dimethylphenylsilane (1 mmol), ethyl acetate (5 mL), RuHAP (0.05 g, Ru: 0.05 mmol), $H_2{}^{18}O$ (10 mmol), 80 °C, O_2 atmosphere, 2h.

RuHAP-catalyzed oxidation of **1** with isotopic $H_2{}^{18}O$ led to the selective formation of ^{18}O-labeled silanol in a quantitative yield (Scheme 1). The oxygen atom incorporated into silanol is not derived from molecular oxygen but from water. In addition, the molar ratio of O_2 uptake to silanol **2** yield was 1:2. A plausible mechanism for this silane oxidation is proposed as follows. Initially, ligand exchange between a silane and a surface Cl moiety of RuHAP gives a silyl-metal intermediate, which undergoes nucleophilic attack by water to produce the corresponding silanol and a Ru–H species. Reaction of the hydride species with molecular oxygen affords a Ru–OOH species, followed by ligand exchange with the silane to regenerate the silyl-metal intermediate together with formation of O_2 and H_2O.§ The inversion of the stereochemistry of silane in the oxidation shows that the nucleophilic attack of water occurs from the backside of a Ru–silicon bond.[2,10]

In summary, RuHAP was found to offer an efficient heterogeneous catalyst system for the oxidation of silanes employing a combined oxidant of water and molecular oxygen. The oxidation proceeded selectively with functional group tolerance. The spent RuHAP catalyst was recyclable with retention of the high activity and selectivity. We are continuing to design functionalized hydroxyapatite catalysts with the aim of developing environmentally benign chemical processes.

Experimental

Procedure for the RuHAP-catalyzed silane oxidation

Into a reaction vessel equipped with a reflux condenser were successively placed RuHAP (0.2 g, Ru^{3+}: 0.2 mol %), ethyl acetate (50 mL), dimethylphenylsilane (100 mmol), and water (200 mmol). The reaction mixture was stirred at 80 °C under atmospheric O_2 pressure. After 6 h, RuHAP was separated by filtration and the organic layer was distilled to afford pure dimethylphenylsilanol (94% isolated yield). The product was identified by mass spectrometry and its^{1}H NMR spectrum.

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† Reaction of (+)-methylethylphenylsilane: the optically active (+)-methylethylphenylsilane (ee 98%) was obtained from racemic methylethylphenylsilane by preparative HPLC (Daicel Chiralcel OJ-H × 2, *n*-hexane, 1.0 mL min^{-1}, 0 °C, 254 nm, t_{RS} = 13.1 min). Into a reaction vessel equipped with a reflux condenser were successively placed RuHAP (0.01 g), 1,4-dioxane (4 mL), 0.1 mol L^{-1} of (+)-methylethylphenylsilane in *n*-hexane solution (1 mL), and water (1 mmol). After the reaction mixture was stirred at 80 °C under O_2 atmosphere for 24 h, RuHAP was separated by filtration. To the filtrate was added $LiAlH_4$ (0.3 mmol) solution in 1,4-dioxane (2 mL), followed by stirring at 90 °C for 24 h to afford (−)-methylethylphenylsilane (ee 97%, determined by HPLC, t_{RS} = 14.2 min). It is known that the reduction of silanols using $LiAlH_4$ proceeds with a retention of stereochemistry.[9]

‡ The Ru K-edge XANES spectrum of the recovered RuHAP catalyst was similar to that of the fresh one and the EXAFS analysis showed no Ru–Ru bond. These results support notion that the Ru species exists as a Ru^{3+} monomer even in the used RuHAP. No chlorine was confirmed by XPS analysis of the used RuHAP, whereas the atomic ratio of Ru to Cl was 1:1 in the fresh RuHAP. Hence, we think that the Cl^- ligand of RuHAP was exchanged with OH^- during the silane oxidation.

§ Hydrolytic oxidation of silanes using the homogeneous $[RuCl_2(p\text{-cymene})]_2$ catalyst is moderately promoted under an oxygen atmosphere.[2] The above oxidation proceeds *via* the oxidative addition of silane to ruthenium, while the catalytic pathway with RuHAP is initiated by the ligand exchange with silane. We think that this unique activation of the Si–H bond using RuHAP is attributed to robust monomeric Ru^{3+} species generated on solid surfaces.

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